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(11) **EP 0 994 138 A1**

(12)

# EUROPEAN PATENT APPLICATION

(43) Date of publication:  
19.04.2000 Bulletin 2000/16

(51) Int. Cl.<sup>7</sup>: **C08G 18/28, C08G 18/10**

(21) Application number: 99119080.2

(22) Date of filing: 01.10.1999

(84) Designated Contracting States:  
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE**  
Designated Extension States:  
**AL LT LV MK RO SI**

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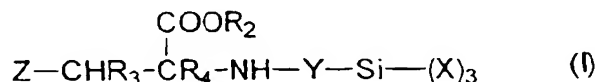
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(54) **Moisture-curable compounds containing isocyanate and alkoxysilane groups**

(57) The present invention relates to moisture-curable compounds which

- a) have an isocyanate group content (calculated as NCO, MW 42) of 0.2 to 30% by weight and an alkoxysilane group content (calculated as Si, MW 28) of 0.2 to 4.5% by weight,
- b) optionally contain repeating ethylene oxide units and
- c) have an equivalent ratio of isocyanate groups to alkoxy groups, which are bound to Si, of 1.0:0.05 to 1.0:1.4,

wherein the preceding percentages are based on the weight of the moisture-curable compounds and wherein the alkoxysilane groups are incorporated as the reaction products of polyisocyanates with amino compounds corresponding to formula I



The present invention also relates to coating, adhesive or sealing compositions containing these moisture-curable compounds as the binder.

EP 0 994 138 A1

## Description

BACKGROUND OF THE INVENTION5 Field of the Invention

[0001] The present invention relates to moisture-curable compounds containing aromatically-bound isocyanate groups and alkoxy silane groups incorporated through aspartate groups, which can be cured in the presence of moisture to form coatings, adhesives and sealants.

10 Description of the Prior Art

[0002] It is known that polyisocyanate resins are curable in the presence of atmospheric moisture to form polyurea coatings. During the curing mechanism an isocyanate group reacts with moisture to form an amino group, which then reacts with another isocyanate group to form a urea group. Even though the polyisocyanate resins possess good adhesion to substrates, there are applications where an improvement in adhesion is needed. In addition, even though moisture-curable resins based on aromatic polyisocyanates have reasonably fast dry times, there is always a need to improve the cure rate of these resins.

[0003] It has been suggested in U.S. Patents 3,420,800 and 3,567,692 that the curing rate of moisture-curable polyisocyanates can be increased by incorporating either aldimines or ketimines. It is stated that the reaction of moisture with an aldimine or ketimine to form the corresponding amine is faster than the reaction of moisture with an isocyanate group to form an amine. A disadvantage of the use of aldimines and ketimines to accelerate the cure of polyisocyanates is that it requires the preparation of an additional component and requires some type of metering equipment to ensure that the two components are blended in the proper proportions.

[0004] It is an object of the present invention to provide compositions having good adhesion to substrates and which cure rapidly to form high quality coatings.

[0005] This object may be achieved with the polyisocyanates according to the present invention, which have been modified to contain alkoxy silane silane groups incorporated through aspartate groups. The fact that it is possible to maintain or even increase the cure rates in accordance with the present invention is surprising because alkoxy silane groups, which are also curable in the presence of moisture, cure more slowly than polyisocyanates. However, when both isocyanate groups and alkoxy silane groups are present, the combination of curing rate and surface appearance is improved.

[0006] Copending application, U.S. Serial No. 09/058,072, discloses water dispersible compounds containing isocyanate and alkoxy silane groups. The water dispersible compounds must be prepared from a polyisocyanate component having a minimum average functionality of 2.4 and be rendered water dispersible by the use of either ionic or nonionic hydrophilic groups.

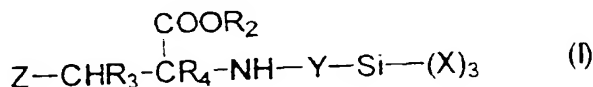
[0007] Copending application, U.S. Serial No. 08/992,163, discloses the preparation of polyurethane-urea dispersions containing alkoxy silane groups incorporated through aspartate groups. However, because the resulting polyurethane dispersions are dispersed in water, they do not contain any unreacted isocyanate groups.

40 SUMMARY OF THE INVENTION

[0008] The present invention relates to moisture-curable compounds which have

- a) a content of aromatically-bound isocyanate groups (calculated as NCO, MW 42) of 0.2 to 30% by weight,
- b) a content of alkoxy silane groups (calculated as Si, MW 28) of 0.2 to 4.5% by weight and
- c) an equivalent ratio of aromatically-bound isocyanate groups to alkoxy groups, which are bound to Si, of 1.0:0.05 to 1.0:1.4,

wherein the preceding percentages are based on the weight of the moisture-curable compounds and wherein the alkoxy silane groups are incorporated as the reaction products of polyisocyanates with amino compounds corresponding to formula I



wherein

- 10 X represents identical or different organic groups which are inert to isocyanate groups below 100°C, provided that at least one of these groups is an alkoxy group,  
 Y represents a linear or branched alkylene radical containing 1 to 8 carbon atoms,  
 Z represents COOR<sub>1</sub> or an aromatic ring,  
 15 R<sub>1</sub> and R<sub>2</sub> are identical or different and represent organic groups which are inert to isocyanate groups at a temperature of 100°C or less and  
 R<sub>3</sub> and R<sub>4</sub> are identical or different and represent hydrogen or organic groups which are inert to isocyanate groups at a temperature of 100°C or less.

20 [0009] The present invention also relates to coating, adhesive or sealing compositions containing these moisture-curable compounds as the binder.

#### DETAILED DESCRIPTION OF THE INVENTION

25 [0010] The compounds according to the present invention are based on the reaction products of polyisocyanates, preferably NCO prepolymers, containing aromatically-bound isocyanate groups and compounds containing alkoxy-silane groups and aspartate groups.

[0011] The moisture-curable compounds have

- 30 a) an isocyanate group content (calculated as NCO, MW 42) of 0.2 to 30% by weight, preferably 0.5 to 20% by weight and more preferably 1.0 to 15% by weight and  
 b) an alkoxy-silane group content (calculated as Si, MW 28) of 0.2 to 4.5% by weight, preferably 0.2 to 4% and more preferably 0.5 to 3.5%.

wherein the preceding percentages are based on the weight of the moisture-curable compounds.

35 [0012] Suitable compounds containing alkoxy-silane groups and amino groups, which may be used to prepare the moisture-curable compounds, include those corresponding to formula I wherein

- X represents identical or different organic groups which are inert to isocyanate groups below 100°C, provided that at least one of these groups is an alkoxy group, preferably alkyl or alkoxy groups having 1 to 4  
 40 carbon atoms and more preferably alkoxy groups,  
 Y represents a linear or branched alkylene radical containing 1 to 8 carbon atoms, preferably a linear radical containing 2 to 4 carbon atoms or a branched radical containing 5 to 6 carbon atoms, more preferably a linear radical containing 3 carbon atoms,  
 Z represents COOR<sub>1</sub> or an aromatic ring, preferably COOR<sub>1</sub>,  
 45 R<sub>1</sub> and R<sub>2</sub> are identical or different and represent organic groups which are inert to isocyanate groups at a temperature of 100°C or less, preferably alkyl groups having 1 to 9 carbon atoms, more preferably methyl, ethyl or butyl groups, and  
 R<sub>3</sub> and R<sub>4</sub> are identical or different and represent hydrogen or organic groups which are inert to isocyanate groups at a temperature of 100°C or less, preferably hydrogen.

50 [0013] Especially preferred are compounds in which X represents methoxy, ethoxy groups or propoxy groups, more preferably methoxy or ethoxy groups and most preferably methoxy groups.

[0014] The compounds of formula I are prepared by reacting aminoalkyl alkoxy-silanes corresponding to formula II



55 with maleic, fumaric or cinnamic acid esters corresponding to formula III



(III)

[0015] Examples of suitable aminoalkyl alkoxysilanes of formula II include 2-aminoethyl-dimethylmethoxy-silane, 6-aminoethyl-tributoxysilane; 3-aminopropyl-trimethoxysilane; 3-aminopropyl-triethoxysilane; 3-aminopropyl-methyldiethoxysilane; 5-aminopentyl-trimethoxysilane; 5-aminopentyl-triethoxysilane, 3-aminopropyl-triisopropoxysilane and 4-amino-3,3-dimethylbutyldimethoxymethylsilane. 4-amino-3,3-dimethylbutyldimethoxymethylsilane is preferred and 3-aminopropyl-trimethoxysilane and 3-aminopropyl-triethoxysilane are especially preferred.

[0016] Examples of optionally substituted maleic, fumaric or cinnamic acid esters suitable for use in the preparation of the polyaspartates include dimethyl, diethyl, dibutyl (e.g., di-n-butyl), diamyl, di-2-ethylhexyl esters and mixed esters based on mixture of these and/or other alkyl groups of maleic acid and fumaric acid; the methyl, ethyl and butyl esters of cinnamic acid; and the corresponding maleic, fumaric and cinnamic acid esters substituted by methyl in the 2- and/or 3-position. The dimethyl, diethyl and dibutyl esters of maleic acid are preferred and the diethyl and dibutyl esters are especially preferred.

[0017] The reaction of primary amines with maleic, fumaric or cinnamic acid esters to form the aspartates of formula I is known and described, e.g. in U.S. Patent 5,364,955, which is herein incorporated by reference. The preparation of the aspartates may be carried out, for example, at a temperature of 0 to 100°C using the starting materials in such proportions that at least 1, preferably 1, olefinic double bond is present for each primary amino group. Excess starting materials may be removed by distillation after the reaction. The reaction may be carried out with or without a solvent, but the use of a solvent is less preferred. If a solvent is used, dioxane is an example of a suitable solvent. The compounds of formula I are colorless to pale yellow. They may be reacted with the polyisocyanate component to form the compounds containing urea and alkoxysilane groups without further purification.

[0018] Suitable polyisocyanates for preparing the compounds containing urea and alkoxysilane groups are selected from monomeric diisocyanates, polyisocyanate adducts and NCO prepolymers, preferably NCO prepolymers. The polyisocyanates contain aromatically-bound isocyanate groups and have an average functionality of 1.5 to 6. The monomeric diisocyanates and polyisocyanate adducts preferably have an average functionality of 1.8 to 6, more preferably 2 to 6 and most preferably 2 to 4. The NCO prepolymers preferably have an average functionality of 1.5 to 4.5, more preferably 1.7 to 3.5 and most preferably 1.8 to 3.2.

[0019] Suitable monomeric diisocyanates may be represented by the formula



wherein R represents an organic group obtained by removing the aromatically-bound isocyanate groups from an organic diisocyanate having a molecular weight of about 160 to 1,000, preferably about 160 to 400. Diisocyanates preferred for the process according to the invention are those in which R represents a divalent aromatic hydrocarbon group having 6 to 15 carbon atoms.

[0020] Examples of the suitable aromatic diisocyanates include 1,3- and/or 1,4-phenylene diisocyanate, 2,4- and/or 2,6-toluylene diisocyanate, 2,4- and/or 4,4'-diphenylmethane diisocyanate, 1,5-diisocyanato naphthalene and mixtures thereof. Polyisocyanates containing 3 or more isocyanate groups, such as 4,4''-triphenylmethane triisocyanate and polyphenyl polymethylene polyisocyanates obtained by phosgenating aniline/formaldehyde condensates may also be used. Preferred aromatic diisocyanates include 2,4- and/or 2,6-toluylene diisocyanate, and 2,4- and/or 4,4'-diphenylmethane diisocyanate.

[0021] In accordance with the present invention the aromatic polyisocyanate component may also be in the form of a polyisocyanate adduct. Suitable polyisocyanate adducts are those containing isocyanurate, uretdione, biuret, urethane, allophanate, carbodiimide and/or oxadiazinetrione groups. The polyisocyanates adducts, which preferably have an NCO content of 5 to 30%, include:

1) Isocyanurate group-containing polyisocyanates which may be prepared as set forth in DE-PS 2,616,416 or in U.S. Patents 3,996,223 and 4,115,373. The isocyanato-isocyanurates generally have an average NCO functionality of 3 to 3.5 and an NCO content of 5 to 30%, preferably 10 to 25% and most preferably 15 to 25% by weight.

2) Uretidione diisocyanates which may be prepared by oligomerizing a portion of the isocyanate groups of a diisocyanate in the presence of a suitable catalyst, e.g., a trialkyl phosphine catalyst, and which may be used in admixture with other aliphatic and/or cycloaliphatic polyisocyanates, particularly the isocyanurate group-containing polyisocyanates set forth under (1) above.

3) Biuret group-containing polyisocyanates which may be prepared according to the processes disclosed in U.S. Patent Nos. 3,124,605; 3,358,010; 3,644,490; 3,862,973; 3,906,126; 3,903,127; 4,051,165; 4,147,714; or 4,220,749 by using co-reactants such as water, tertiary alcohols, primary and secondary monoamines, and primary and/or secondary diamines. These polyisocyanates preferably have an NCO content of 18 to 22% by weight

and an average NCO functionality of 3 to 3.5.

4) Urethane group-containing polyisocyanates which may be prepared in accordance with the process disclosed in U.S. Patent No. 3,183,112 by reacting excess quantities of polyisocyanates preferably diisocyanates, with low molecular weight glycols and polyols having molecular weights of less than 400, such as trimethylol propane, glyc-  
erine, 1,2-dihydroxy propane and mixtures thereof. The urethane group-containing polyisocyanates have a most  
5 preferred NCO content of 12 to 20% by weight and an (average) NCO functionality of 2.5 to 3

5) Allophanate group-containing polyisocyanates which may be prepared according to the processes disclosed in U.S. Patent Nos. 3,769,318, 4,160,080 and 4,177,342. The allophanate group-containing polyisocyanates have a  
most preferred NCO content of 12 to 21% by weight and an (average) NCO functionality of 2 to 4.5.

6) Isocyanurate and allophanate group-containing polyisocyanates which may be prepared in accordance with the  
10 processes set forth in U.S. Patents 5,124,427, 5,208,334 and 5,235,018, the disclosures of which are herein incor-  
porated by reference, preferably polyisocyanates containing these groups in a ratio of monoisocyanurate groups to  
mono-allophanate groups of about 10:1 to 1:10, preferably about 5:1 to 1:7.

7) Carbodiimide group-containing polyisocyanates which may be prepared by oligomerizing di- or polyisocyanates  
15 in the presence of known carbodiimidization catalysts as described in DE-PS 1,092,007, US-PS 3,152,162 and DE-  
OS 2,504,400, 2,537,685 and 2,552,350.

8) Polyisocyanates containing oxadiazinetrione groups and containing the reaction product of two moles of a diiso-  
cyanate and one mole of carbon dioxide.

20 **[0022]** Preferred polyisocyanate adducts are those containing isocyanurate groups, biuret groups, allophanate  
groups and/or uretdione groups.

**[0023]** The NCO prepolymers, which may also be used as the polyisocyanate component in accordance with the  
present invention, are prepared from the previously described monomeric polyisocyanates or polyisocyanate adducts,  
preferably monomeric diisocyanates, and organic compounds containing at least two isocyanate-reactive groups, pref-  
erably at least two hydroxy groups. These organic compounds include high molecular weight compounds having molec-  
25 ular weights of 500 to about 10,000, preferably 800 to about 8,000, and more preferably 1800 to 8,000, and optionally  
low molecular weight compounds having molecular weights below 500. The molecular weights are number average  
molecular weights ( $M_n$ ) and are determined by end group analysis (OH and/or NH number). Products obtained by react-  
ing polyisocyanates exclusively with low molecular weight compounds are polyisocyanates adducts containing ure-  
thane groups and are not considered to be NCO prepolymers.

**[0024]** Examples of the high molecular weight compounds are polyester polyols, polyether polyols, polyhydroxy  
polycarbonates, polyhydroxy polyacetals, polyhydroxy polyacrylates, polyhydroxy polyester amides and polyhydroxy  
polythioethers. The polyester polyols, polyether polyols and polyhydroxy polycarbonates are preferred, especially the  
polyether polyols.

35 **[0025]** Examples of suitable high molecular weight polyhydroxyl compounds include polyester polyols prepared  
from low molecular weight alcohols and polybasic carboxylic acids such as adipic acid, sebacic acid, phthalic acid, iso-  
phthalic acid, tetrahydrophthalic acid, hexahydrophthalic acid, maleic acid, the anhydrides of these acids and mixtures  
of these acids and/or acid anhydrides. Polylactones having hydroxyl groups, particularly poly- $\epsilon$ -caprolactone, are also  
suitable for producing the prepolymers.

40 **[0026]** Also suitable for preparing the prepolymers are polyether polyols, which may be obtained in known manner  
by the alkoxylation of suitable starter molecules. Examples of suitable starter molecules include polyols, water, organic  
polyamines having at least two N-H bonds and mixtures thereof. Suitable alkylene oxides for the alkoxylation reaction  
are preferably ethylene oxide and/or propylene oxide, which may be used in sequence or in admixture.

**[0027]** Other suitable polyols include polycarbonates having hydroxyl groups, which may be produced by the reac-  
45 tion of diols with phosgene or diaryl carbonates such as diphenyl carbonate.

**[0028]** Further details concerning the low molecular weight compounds and the starting materials and methods for  
preparing the high molecular weight polyhydroxy compounds are disclosed in U.S. Patent 4,701,480, herein incorpo-  
rated by reference.

50 **[0029]** Other examples include the known high molecular weight amine-functional compounds, which may be pre-  
pared by converting the terminal hydroxy groups of the polyols previously described to amino groups, and the high  
molecular weight polyaspartates and polyaldimines disclosed in U.S. Patents 5,243,012 and 5,466,771, respectively,  
herein incorporated by reference.

**[0030]** These NCO prepolymers preferably have an isocyanate content of 0.3 to 35% by weight, more preferably  
0.6 to 25% by weight and most preferably 1.2 to 20% by weight. The NCO prepolymers are produced by reacting the  
diisocyanates with the polyol component at a temperature of 40 to 120°C, preferably 50 to 100°C, at an NCO/OH equiv-  
55 alent ratio of 1.3:1 to 20:1, preferably 1.4:1 to 10:1. If chain extension via urethane groups is desired during the prepa-  
ration of the isocyanate prepolymers, an NCO/OH equivalent ratio of 1.3:1 to 2:1 is selected. If chain extension is not  
desired, an excess of diisocyanate is preferably used, corresponding to an NCO/OH equivalent ratio of 4:1 to 20:1, pref-

erably 5:1 to 10:1. The excess diisocyanate may optionally be removed by thin layer distillation when the reaction is completed. In accordance with the present invention NCO prepolymers also include NCO semi-prepolymers which contain unreacted starting polyisocyanates in addition to the urethane group-containing prepolymers.

[0031] The moisture-curable compounds according to the invention are prepared by reacting the polyisocyanate component with the amino-functional silanes in an amount sufficient such that the moisture-curable compounds contain isocyanate groups and alkoxy groups, which are bound to Si, in an equivalent ratio of 1.0:0.05 to 1.0:1.4, preferably 1.0:0.05 to 1.0:1.2 and more preferably 1.0:0.1 to 1.0:1.0.

[0032] The moisture-curable compounds of the present invention cannot be stably dispersed in water, either in the form of an oil-in-water emulsion or a water-in-oil emulsion, without settling, coagulation or separation.

[0033] The reaction is preferably carried out by incrementally adding the isocyanate-reactive compound containing alkoxysilane groups to the polyisocyanate.

[0034] The compounds according to the invention can also be prepared by blending different types of compounds, provided that they satisfy the preceding guidelines regarding the amounts hydrophilic groups, alkoxysilane groups and isocyanate groups. For example, compounds which contain alkoxysilane groups, but are free from isocyanate groups, and/or compounds which contain isocyanate groups, but which do not contain alkoxysilane groups, may be present as a portion of the compounds according to the invention.

[0035] If compounds containing both alkoxysilane groups and isocyanate groups are prepared, then it is preferred that at least a portion of the polyisocyanate starting material is an NCO prepolymer, although polyisocyanate monomers and/or adducts may be used, especially in admixture with NCO prepolymers.

[0036] If mixtures of compounds containing alkoxysilane groups and compounds containing isocyanate groups are used, then it is preferred that at least one of these compounds is based on an NCO prepolymer. For example, an NCO prepolymer may be used in admixture with a silylated polyisocyanate monomer or adduct, or a silylated NCO prepolymer may be used in admixture with a polyisocyanate monomer or adduct. Volatile polyisocyanate monomers should not generally be used in combination with silylated NCO prepolymers, not because such a mixture would not be operative according to the invention, but rather because of the known difficulties of using volatile polyisocyanates in monomeric form.

[0037] Even though it is preferred that one of compounds to be blended is an NCO prepolymer, it is not necessary to always use an NCO prepolymer. Blends of silylated and non-silylated polyisocyanate monomers and adducts may be used in accordance with the present invention.

[0038] The reaction between the polyisocyanate component and the compounds containing alkoxysilane groups to form the urea groups is conducted at a temperature of 10 to 100°C, preferably 20 to 80°C and more preferably 20 to 50°C.

[0039] In accordance with the present invention the special type of urea groups formed by the reaction of the amino-functional compounds containing alkoxysilane groups and aspartate groups with the polyisocyanate component may be converted to hydantoin groups in known manner by heating the compounds at elevated temperatures, optionally in the presence of a catalyst. Therefore, the term "urea groups" is also intended to include other compounds containing the group, N-CO-N, such as hydantoin groups.

[0040] The formation of hydantoin groups is not preferred in accordance with the present invention because this reaction also results in the formation of a monoalcohol, which will react with the isocyanate groups without chain extension. For this reason it is preferred to form the urea groups at low temperatures to avoid the formation of hydantoin groups. However, since hydantoin groups can also be formed under ambient conditions during storage, it is preferred to use the products of the invention shortly after their preparation.

[0041] The compounds of the present invention are suitable for use in one-component, coating, adhesive or sealing compositions, which can be cured in the presence of atmospheric moisture. The compositions cure by a dual cure mechanism, i.e.,

- 1) by the reaction of isocyanate groups with moisture and
- 2) by "silane polycondensation" from the hydrolysis of alkoxysilane groups to form Si-OH groups and their subsequent reaction with either Si-OH or Si-OR groups to form siloxane groups (Si-O-Si) and
- 3) conceivably by the reaction of isocyanate groups with Si-OH groups.

[0042] Suitable acidic or basic catalysts may be used to promote the curing reaction. Examples include acids such as paratoluene sulfonic acid; metallic salts such as dibutyl tin dilaurate; tertiary amines such as triethylamine or triethylene diamine; and mixtures of these catalysts. Low molecular weight, basic aminoalkyl trialkoxysilanes, such as those represented by formula II, also accelerate hardening of the compounds according to the invention.

[0043] The one-component compositions generally may be either solvent-free or contain up to 70%, preferably up to 60% organic solvents, based on the weight of the one-component composition, depending upon the particular application. Suitable organic solvents include those which are known from polyurethane chemistry.

[0044] The compositions may also contain known additives, such as leveling agents, wetting agents, flow control agents, antiskinning agents, antifoaming agents, fillers (such as silica, aluminum silicates and high-boiling waxes), viscosity regulators, plasticizers, pigments, dyes, UV absorbers and stabilizers against thermal and oxidative degradation.

[0045] The one-component compositions may be applied to any desired substrates, such as wood, plastics, leather, paper, textiles, glass, ceramics, plaster, masonry, metals and concrete. They may be applied by standard methods, such as spray coating, spread coating, flood coating, casting, dip coating and roll coating. The coating compositions may be clear or pigmented lacquers. Suitable pigments include the known inorganic and organic pigments, especially the inorganic pigments, such as titanium dioxide and the iron oxides.

[0046] The one-component compositions may be cured at ambient temperature or at elevated temperatures. Preferably, the moisture-curable resins are cured at ambient temperatures.

[0047] The invention is further illustrated but is not intended to be limited by the following examples in which all parts and percentages are by weight unless otherwise specified.

## EXAMPLES

### Polyether 1

[0048] A polyether polyol prepared by the alkoxylation of propylene glycol with a 91/9 mixture of propylene and ethylene oxide and having a molecular weight of 2000.

### Silane Aspartate 1 - N-(3-trimethoxysilylpropyl) aspartic acid diethyl ester

[0049] 1438 parts (8.27 equiv.) of 3-aminopropyltrimethoxysilane were added to a 5 liter flask fitted with agitator, thermocouple, nitrogen inlet and addition funnel with condenser. 1423.2 parts (8.27 equiv.) of diethyl maleate were added dropwise over a period of 2 hours. The temperature of the reactor was maintained at 25°C during the addition. The reactor was maintained at 25°C for an additional 5 hours at which time the product was poured into glass containers and sealed under a blanket of nitrogen. After one week the unsaturation number was 0.6 indicating the reaction was ~99% complete. The product, N-(3-trimethoxysilylpropyl) aspartic acid diethyl ester, had a viscosity of 11 mPa.s at 25°C.

### Polyisocyanate-based resin 1 containing isocyanate groups (Comparison)

[0050] 1156 parts (8.972 equiv.) of an aromatic polyisocyanate mixture (Mondur MRS-4, available from Bayer Corporation, a mixture of 4,4'-and 2,4'-diphenylmethane diisocyanate and higher homologs thereof) were added to a three liter flask equipped with stirrer, nitrogen inlet, heater and thermometer. 839 parts (0.419 equiv.) of polyether 2 was added over a 3.5 hour period. The reaction mixture was heated to 60°C and maintained at that temperature for 14.5 hours. 5.33 parts (0.060 equiv.) of dimethylaminoethanol was then added and the reaction mixture was maintained at 60°C for an additional 7.5 hours until the NCO content was 17.80% (theoretical NCO 17.83%).

### Polyisocyanate-based resin 2 containing isocyanate and silane groups

[0051] 255.8 parts (1.00 equiv.) of polyisocyanate resin 1 were added to a 1 liter flask equipped with stirrer, nitrogen inlet, heater and thermometer. 73.2 parts (0.20 equiv.) of silane aspartate 1 were added and the reaction mixture was heated to and held at 60°C for 31 hours.

### Polyisocyanate-based resin 3 containing isocyanate and silane groups

[0052] 255.8 parts (1.00 equiv.) of polyisocyanate resin 1 were added to a 1 liter flask equipped with stirrer, nitrogen inlet, heater and thermometer. 91.5 parts (0.25 equiv.) of silane aspartate 1 were added and the reaction mixture was heated to and held at 60°C for 31 hours.

### Polyisocyanate-based resin 4 containing isocyanate and silane groups

[0053] 255.8 parts (1.00 equiv.) of polyisocyanate resin 1 were added to a 1 liter flask equipped with stirrer, nitrogen inlet, heater and thermometer. 109.8 parts (0.30 equiv.) of silane aspartate 1 were added and the reaction mixture was heated to and held at 60°C for 31 hours.

## EP 0 994 138 A1

### Polyisocyanate-based resin 5 containing silane groups (Comparison)

**[0054]** 127.5 parts (0.50 equiv.) of polyisocyanate resin 1 were added to a 1 liter flask equipped with stirrer, nitrogen inlet, heater and thermometer. 183 parts (0.50 equiv.) of silane aspartate 1 were added and the reaction mixture was heated to and held at 60°C for 31 hours.

### Polyisocyanate-based resin 6 containing isocyanate groups (Comparison)

**[0055]** A commercially available NCO prepolymer prepared from 4,4'-diphenylmethane diisocyanate and a polyether and having an NCO content of 8.0 % NCO and a viscosity of 6500 mPa.s @ 25°C (available from Bayer Corp. as Desmodur E-28).

### Preparation of coatings from Polyisocyanate-based resins 1-5

**[0056]** Coatings were prepared from polyisocyanate-based resins 1-5. The coating compositions were applied to glass panels with a 3 mil draw down bar and dried at 22°C and 70% relative humidity. Dry times were determined with a Gardner Dry Time Meter as described in the Pacific Scientific Instruction Manuals DG-9600 and DG-9300. The compositions and dry times are set forth in the following table.

Coating prepared from Polyisocyanate-based resin					
	1 (Comp)	2	3	4	5 (Comp)
Resin	20	20	20	20	20
Aromatic 100 solvent	5	5	5	5	0
NCO:Alkoxy Equiv. Ratio	100:0	57:43	50:50	43:57	0:100
Dry Time, min					
ST	2	15	35	190	>5500
SD	5	15	30	300	>5500
HD	10	30	195	>360	>5500
Appearance	Big Bubbles	Small Blisters	Smooth and Glossy	Small Blisters	Film did not dry

### Preparation of pigmented coatings from Polyisocyanate-based resins 5-6

**[0057]** Zinc-rich (pigmented) coatings were prepared from the following formulations:

Formulation	A	B
Aromatic 100 solvent	31.4	31.4
Bentone 34 gel	14.1	14.1
Polyisocyanate-based resin 6	40.0	0.0
Polyisocyanate-based resin 5	0.0	40.0
Zinc Dust 64 <sup>1</sup>	284.0	284.0
p-Toluene Sulfonylisocyanate	3.7	3.7

<sup>1</sup> available from ZCA

**[0058]** Bentone 34 gel was prepared by slowly adding 10 parts of Bentone 34 clay (available from NL Industries)



and 5 parts of Antiterra U surfactant (available from Byk Chemie) to 85 parts of Aromatic 100 solvent under agitation with a Cowles dispersing blade. The gel was blended until smooth.

[0059] Formulations A and B were prepared by blending the ingredients in the above order under agitation with a paddle stirrer. The p-TSI was added slowly and carefully.

[0060] Coatings were made on glass plates with a 3 mil draw down bar at 22°C and 60% relative humidity. Dry times were determined with a Gardner Dry Time Meter as described in the Pacific Scientific Instruction Manuals DG-9600 and DG-9300. The compositions and dry times are set forth in the following table.

Resin Adduct Studies							
Formulation A	10.0	8.0	7.5	7.0	6.0	5.0	0.0
Formulation B	0.0	2.0	2.5	3.0	4.0	5.0	10.0
Dry Time, min							
ST	50	45	30	30	45	30	>360
SD	120	90	75	75	110	120	>360
HD	180	180	170	230	285	190	>360
Appearance	Smooth coating for all samples						

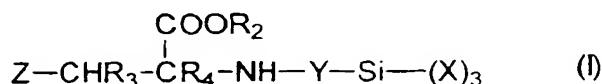
[0061] Although the invention has been described in detail in the foregoing for the purpose of illustration, it is to be understood that such detail is solely for that purpose and that variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention except as it may be limited by the claims.

#### Claims

1. A moisture-curable compound which has

- a) a content of aromatically-bound isocyanate groups (calculated as NCO, MW 42) of 0.2 to 30% by weight,
- b) a content of alkoxyisilane groups (calculated as Si, MW 28) of 0.2 to 4.5% by weight and
- c) an equivalent ratio of aromatically-bound isocyanate groups to alkoxy groups, which are bound to Si, of 1.0:0.05 to 1.0:1.4,

wherein the preceding percentages are based on the weight of the moisture-curable compound and wherein the alkoxyisilane groups are incorporated as the reaction product of a polyisocyanate with an amino compound corresponding to formula I



wherein

- X represents identical or different organic groups which are inert to isocyanate groups below 100°C, provided that at least one of these groups is an alkoxy,
- Y represents a linear or branched alkylene radical containing 1 to 8 carbon atoms,
- Z represents COOR<sub>1</sub> or an aromatic ring,
- R<sub>1</sub> and R<sub>2</sub> are identical or different and represent organic groups which are inert to isocyanate groups at a temperature of 100°C or less and
- R<sub>3</sub> and R<sub>4</sub> are identical or different and represent hydrogen or organic groups which are inert to isocyanate groups at a temperature of 100°C or less.

2. The moisture-curable compound of Claim 1 wherein

- X represents identical or different alkyl or alkoxy groups having 1 to 4 carbon atoms,  
Y represents a linear radical containing 2 to 4 carbon atoms or a branched radical containing 5 to 6 carbon atoms,  
Z represents COOR<sub>1</sub>,  
5 R<sub>1</sub> and R<sub>2</sub> are identical or different and represent alkyl groups having 1 to 9 carbon atoms and  
R<sub>3</sub> and R<sub>4</sub> represent hydrogen.

3. The moisture-curable compound of Claim 1 wherein

- 10 X represents identical or different alkoxy groups having 1 to 4 carbon atoms,  
Y represents a linear radical containing 2 to 4 carbon atoms or a branched radical containing 5 to 6 carbon atoms,  
Z represents COOR<sub>1</sub>,  
R<sub>1</sub> and R<sub>2</sub> are identical or different and represent methyl, ethyl or butyl and  
15 R<sub>3</sub> and R<sub>4</sub> represent hydrogen.

4. The moisture-curable compound of Claim 1 wherein at least a portion of said polyisocyanate is an NCO prepolymer.

20 5. The moisture-curable compound of Claim 2 wherein at least a portion of said polyisocyanate is an NCO prepolymer.

6. The moisture-curable compound of Claim 3 wherein at least a portion of said polyisocyanate is an NCO prepolymer.

25 7. The moisture-curable compound of Claim 1 which comprises a blend of a polyisocyanate-based resin that contains alkoxysilane groups and is substantially free from isocyanate groups and a polyisocyanate-based resin that contains isocyanate groups and is substantially free from alkoxysilane groups, wherein at least one of the polyisocyanate-based resins is an NCO prepolymer.

30 8. The moisture-curable compound of Claim 2 which comprises a blend of a polyisocyanate-based resin that contains alkoxysilane groups and is substantially free from isocyanate groups and a polyisocyanate-based resin that contains isocyanate groups and is substantially free from alkoxysilane groups, wherein at least one of the polyisocyanate-based resins is an NCO prepolymer.

35 9. The moisture-curable compound of Claim 3 which comprises a blend of a polyisocyanate-based resin that contains alkoxysilane groups and is substantially free from isocyanate groups and a polyisocyanate-based resin that contains isocyanate groups and is substantially free from alkoxysilane groups, wherein at least one of the polyisocyanate-based resins comprises an NCO prepolymer.

40 10. The moisture-curable compound of Claim 7 wherein both of the polyisocyanate-based resins comprise NCO prepolymers.

45 11. The moisture-curable compound of Claim 8 wherein both of the polyisocyanate-based resins comprise NCO prepolymers.

12. The moisture-curable compound of Claim 9 wherein both of the polyisocyanate-based resins comprise NCO prepolymers.

50 13. The moisture-curable compound of Claim 1 wherein said moisture-curable compound cannot be stably dispersed in water.

14. The moisture-curable compound of Claim 2 wherein said moisture-curable compound cannot be stably dispersed in water.

55 15. The moisture-curable compound of Claim 3 wherein said moisture-curable compound cannot be stably dispersed in water.

EP 0 994 138 A1

16. The moisture-curable compound of Claim 4 wherein said moisture-curable compound cannot be stably dispersed in water.
17. The moisture-curable compound of Claim 5 wherein said moisture-curable compound cannot be stably dispersed in water.
18. The moisture-curable compound of Claim 6 wherein said moisture-curable compound cannot be stably dispersed in water.
19. The moisture-curable compound of Claim 7 wherein said moisture-curable compound cannot be stably dispersed in water.
20. The moisture-curable compound of Claim 8 wherein said moisture-curable compound cannot be stably dispersed in water.
21. The moisture-curable compound of Claim 9 wherein said moisture-curable compound cannot be stably dispersed in water.
22. The moisture-curable compound of Claim 10 wherein said moisture-curable compound cannot be stably dispersed in water.
23. The moisture-curable compound of Claim 11 wherein said moisture-curable compound cannot be stably dispersed in water.
24. The moisture-curable compound of Claim 12 wherein said moisture-curable compound cannot be stably dispersed in water.
25. A one-component coating, adhesive or sealant composition wherein the binder comprises the moisture-curable compound of Claim 1.



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# EUROPEAN SEARCH REPORT

Application Number  
EP 99 11 9080

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	EP 0 831 108 A (OSI SPECIALTIES, INC.) 25 March 1998 (1998-03-25) * page 4, line 55 - line 56; claim 1 *	1-6, 13-18,25	C08G18/28 C08G18/10
X	EP 0 864 575 A (BAYER CORP.) 16 September 1998 (1998-09-16) * page 6, line 26 - line 36; claims 1-3,13 *	1-6, 13-18,25	
A	WO 98 18843 A (3M) 7 May 1998 (1998-05-07) * page 8, line 9 - page 9, line 4; claim 1 *	1-6, 13-18,25	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			C08G
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 28 January 2000	Examiner Angiolini, D
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EPO FORM 1503 03 82 (P04001)

**ANNEX TO THE EUROPEAN SEARCH REPORT  
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EP 99 11 9080

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The members are as contained in the European Patent Office EDP file on  
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28-01-2000

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For more details about this annex see Official Journal of the European Patent Office, No. 12/82

